Filter pore size selection for characterizing dissolved organic carbon and trihalomethane precursors from soils

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Abstract

Filters with a pore size of 0.45 μm have been arbitrarily used for isolating dissolved organic carbon (DOC) in natural waters. This operationally defined DOC fraction often contains heterogeneous organic carbon compounds that may lead to inconsistent results when evaluating trihalomethane formation potential (THMFP). A finer pore size filter provides more homogeneous DOC properties and enables a better characterization of organic matter. In this study, we examined the effects of filter pore size (1.2, 0.45, 0.1 and 0.025 μm) on characterizing total organic carbon, ultra-violet absorbance at 254 nm (UV_{254}) and THMFP of water extracts from a mineral and organic soil in the Sacramento-San Joaquin Delta, California. Results showed that the majority of water extractable organic carbon (WEOC) from these soils was smaller than 0.025 μm, 85% and 57% in organic and mineral soils, respectively. A high proportion of colloidal organic carbon (COC) in mineral soil extracts caused water turbidity and resulted in an abnormally high UV_{254} in 1.2 and 0.45 μm filtrates. The reactivity of organic carbon fractions in forming THM was similar for the two soils, except that COC from the mineral soil was about half that of others. To obtain a more homogeneous solution for characterizing THM precursors, we recommend a 0.1 μm or smaller pore-size filter, especially for samples with high colloid concentrations.
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1. Introduction

The Sacramento-San Joaquin Delta is a source of drinking water for 22 million people in California, USA. There is a significant increase in organic carbon when water passes through the Delta. High organic carbon in water is of concern because it is a precursor of carcinogenic disinfection by-products, such as trihalomethane (THM). The increase in organic carbon or THM precursors in Delta waters is partially attributed to agricultural drainage in the Delta, which is estimated to contribute an average of $36\,Mg\,C\,day^{-1}$ into Delta waterways (Amy et al., 1990; Jassby and Cloern, 2000). Organic-rich peat soils in the area have been identified as a major source of organic carbon and THM precursors in the drainage waters (California Department of Water Resources, 1994; Fujii et al., 1998). Thus, understanding the chemical characteristics of organic carbon leaching

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from Delta soils is essential for water treatment facilities that use Delta waters as a drinking water source.

Conventional filtration commonly uses a 0.45 µm pore size filter as a cutoff point for defining dissolved organic carbon (DOC). However, a pore size of 0.45 µm is so large on a colloidal scale that heterogeneous organic fractions possibly exist in 0.45 µm filtrates (Thurman, 1985). Studies have shown that different size organic matter fractions, such as particulate organic matter, colloidal organic matter, and dissolved organic matter have different chemical properties (Guo et al., 2003). We speculate that these fractions may also have different reactivity in forming THM during chlorination. Importantly, inconsistent results have been observed in THM research when using 0.45 µm filtrates (Chow et al., submitted). The heterogeneity in 0.45 µm filtrates is probably one of the main reasons for the inconclusive results. While most research focuses on THM precursors in the <0.45 µm fraction (Owen et al., 1993), a recent study showed that suspended organic matter from soil extracts likely serves as an important pool of THM precursors (Li et al., 2003). The reactivity from organic matter >0.45 µm in THM formation has seldom been studied. Thus, organic matter should be further divided into more homogeneous fractions for analysis. One objective of this study was to evaluate THM reactivity and chemical characteristics of filtrates from different pore-size filters with a special focus on application to studies of organic carbon from Delta soils.

The amounts of water extractable organic carbon (WEOC) and THM precursors in soils are probably proportional to the content of soil organic carbon (SOC). Environmental factors and farming practices also control the partitioning of WEOC and THM precursors with SOC. Current agricultural practices in the Sacramento-San Joaquin Delta include intensive summer irrigation and winter flooding. Soil salinity and sodicity increase in summer due to evapotranspiration of soil water, whereas soil salinity and sodicity decrease in winter due to salt leaching. The change in soil water composition affects soil chemistry, and eventually affects the amount of WEOC and THM precursors leaching from the soils. A controlled laboratory study conducted by Chow et al. (2003) showed that an increase in salinity significantly decreased DOC concentrations in soil water from agricultural peat soils in the Delta. The specific UV absorbance at 254 nm (SUV_{254}), a surrogate for THM precursors, decreased with an increase in salinity and Ca^{2+} concentrations. This study only examined the dissolved phase of organic soils passing a 0.45 µm filter. Other physical fractions of organic soils as well as organic carbon from mineral soils were not studied. In this study, we further examine salt effects on the solubility of different size organic carbon fractions along with the contributions of organic carbon from a mineral soil. Results from the study contribute to a

better understanding of the role of agricultural soils in the production of THM precursors and the carbon budget of Delta waterways.

2. Materials and methods

2.1. Soil sampling and characterization

Soil samples from Twitchell Island (N38°07′02.3″, W121°38′20.5″) and Webb Tract (N38°04′01.5″, W121°35′41.6′) in the west-central Delta were collected for this study. The soil from Twitchell Island is classified as a Scribner Clay Loam (*Cumulic Endoaquoll*) and the soil from Webb Tract is classified as a Rindge Muck (*Typic Haplosaprist*) (USDA, 1977; USDA, 1993). These two soils were selected because they are representative of major mineral and organic soils in the Delta. Soil samples were colleted from the surface 0–0.3 m depth. Soils were fully mixed in a plastic bag, transferred to a 1 L Mason jar, and frozen until further use. Surface soil was used in this study because a previous study showed that the surface soil zone is the major source of organic carbon and THM precursors in the agricultural drainage (Chow et al., 2003).

2.2. Organic carbon extraction

Deionized water (DW) and synthesized salt solutions were used for organic carbon extraction from the two soils. A Barnstead Type D4700 NANO PURE water purification system equipped with an organic removal cartridge provided >18 MΩ DW. For the synthesized salt solutions, we prepared 0.005 M Ca^{2+} solutions and 0.01 M Na^+ solutions from reagent grade $CaCl_2$ or NaCl. These solutions are equivalent to a specific conductivity (K) of 1 dS m^{-1}. This salinity level was chosen because 1 dS m^{-1} was the median value for K of soil water in a field study (Fujii et al., 1998). Ten grams of dry soil were mixed with 1 L DW, Ca^{2+} or Na^+ solutions in a large glass container to prepare a 1:100 (w:v) extraction. The soil-solution mixture was stirred for 2 h at room temperature (20 ± 1 °C). The mixture was transferred to glass centrifuge tubes and centrifuged for 20 min at 250 g relative centrifugal force. The supernatant was withdrawn and filtered through a series of MF-Millipore mixed cellulose ester membrane filters with four different pore sizes: 1.2, 0.45, 0.1, and 0.025 µm (Fig. 1). Each filter was rinsed with 1 L DW to remove any residual organic contaminants before use (Karanfil et al., 2003). The supernatant was filtered through these filters in series. Particularly, in the filtration using 1.2 and 0.45 µm pore size filters, a new pre-rinsed filter was replaced as soon as any visible water piled up on top of the filters to avoid filter fouling. After each filtration, a portion of filtrate was saved in glass
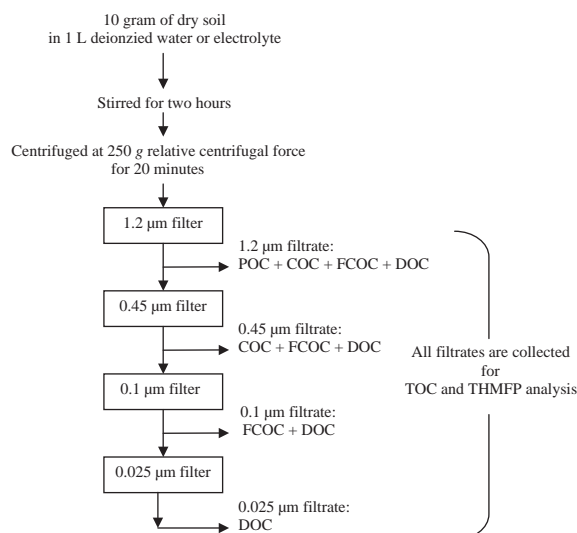
10 gram of dry soil
in 1 L deionzied water or electrolyte

↓

Stirred for two hours

↓

Centrifuged at 250 g relative centrifugal force
for 20 minutes

↓

| 1.2 μm filter |

→ 1.2 μm filtrate:
POC + COC + FCOC + DOC

↓

| 0.45 μm filter |

→ 0.45 μm filtrate:
COC + FCOC + DOC

↓

| 0.1 μm filter |

→ 0.1 μm filtrate:
FCOC + DOC

↓

| 0.025 μm filter |

→ 0.025 μm filtrate:
DOC

All filtrates are collected
for
TOC and THMFP analysis

Fig. 1. Fractionation scheme used in the study. TOC and THMFP of individual organic carbon fractions were determined as the difference between filtrates. POC, COC, FCOC, and DOC are the acronyms of particulate, colloidal, fine colloidal, and dissolved organic carbon, respectively.

containers and refrigerated at 4 °C through completion of chemical analyses. Duplicate samples were obtained for each soil and each extracting solution.

2.3. Soil characterization and chemical analysis

Soil samples were characterized for moisture content, pH, K, SOC, major cations and anions, and cation exchange capacity (CEC). The soil moisture content was determined by drying at 105 °C for 24 h. K and pH were determined on a 1:1, soil:water mixture, according to Environmental Protection Agency (EPA) methods 9050 and 9045C, respectively. SOC was determined by the Walkley Black method (Nelson and Sommers, 1996). Major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and anions (Cl^-, Br^-, NO_3^-, SO_4^{2-}) were determined in a 1:1, soil:water extract by inductively coupled plasma-atomic emission spectrometry and ion exchange chromatography, according to EPA method 6010B and 300, respectively. CEC was determined, according to EPA method 9081, by mixing soil with excess sodium acetate solution and the concentration of displaced sodium determined by atomic absorption emission spectroscopy.

All water extracts were analyzed for total organic carbon (TOC), ultra-violet absorbance at 254 nm (UV_{254}), and THM formation potential (THMFP). TOC was determined by heat-promoted persulfate oxidation, using a TOC analyzer (O.I. Analytical 1010). UV_{254} was determined using a diode array spectrophotometer (Hewlett Packard P8452A). Samples

were diluted to less than $10 mg L^{-1}$ TOC before UV_{254} measurement. The dose-based THMFP method developed by Brtye Laboratory of the California Department of Water Resources was used in this study (California Department of Water Resources, 1994). Briefly, samples were chlorinated with freshly prepared $NaOCl/H_3BO_3$ buffered at pH 8.3 ± 0.1. Each sample was diluted to a TOC value less than $10 mg L^{-1}$ and treated with a constant chlorine dosage ($120 mg L^{-1}$). Samples were stored in a 40 ml borosilicate amber vial and sealed without headspace. All vials satisfied the requirements of EPA Publication #9240.0-05A specifications and guidance for contaminant-free containers. The vials were incubated for 7 days at room temperature ($20 \pm 1 °C$). Following incubations, 0.15 ml of 10% sodium sulfite solution was added to quench residual chlorine. All samples were refrigerated at 4 °C and analyzed within two weeks. Quantification of THM was accomplished using a Hewlett Packard 5890 II gas chromatograph fitted with an auto injector, a capillary split-splitless inlet, a ^{63}Ni electron capture detector, and a RESTEK Rtx-502.2 column ($105 m \times 0.53 mm \times 3 μm$). The GC oven was programmed to hold an initial temperature of 35 °C for 10 min, increased to 140 °C at a rate of $3.5 °C min^{-1}$ and to 220 °C at a rate of $5 °C min^{-1}$, and finally held at 220 °C for 3 min.

3. Results and discussion

3.1. General soil properties—Rindge Muck vs. Scribner Clay Loam

Table 1 presents some general physical and chemical properties of the soils used in this study. First, significant differences in SOC and CEC are noted between the two soils. The Clay Loam contained 4% SOC and had a CEC of 37 meq 100 g soil^{-1}. In contrast, the Rindge Muck had much higher SOC and CEC, 23% and 149 meq 100 g soil^{-1}, respectively. Second, the soil salinity of Rindge Muck ($2.1 dS m^{-1}$) was five times higher than that of the Clay Loam ($0.4 dS m^{-1}$). Although high soil salinity may reduce the amount of organic carbon leaching from soils (Chow et al., 2003), the 1:100, soil:solution ratio should dilute any salt effect resulting in little impact on the extraction process. Third, the particle size analysis showed that both soils had similar proportions of sand, silt and clay in the mineral fraction. Water-soluble cations were dominated by Ca^{2+} and Mg^{2+} and anions by Cl^- and NO_3^-, with SO_4^{2-} also being very high in the Rindge Muck. There was a charge imbalance between measured cations and anions in both soils; however, this imbalance was not due to analytical error. Because some prevalent anionic components were not measured, the imbalance was expected. Other important anions in the charge balance

Table 1
General soil properties of soils used in this experiment

Description	Twitchell Island Scribner Clay Loam	Webb Tract Rindge Muck
Water soluble cations		
Na^+ (mg g^{-1})	0.22	0.68
K^+ (mg g^{-1})	0.92	0.41
Ca^{2+} (mg g^{-1})	4.87	15.24
Mg^{2+} (mg g^{-1})	6.72	3.50
Water soluble anions		
Br^- (mg g^{-1})	<0.01	<0.01
Cl^- (mg g^{-1})	0.18	0.58
NO_3^- (mg g^{-1})	0.11	0.29
SO_4^{2-} (mg g^{-1})	<0.02	1.26
Other properties		
pH	6.41	5.25
K (dS m^{-1})	0.35	2.10
SOC (%)	3.7	22.9
Soil CEC (meq 100 g^{-1})	36.6	148.7
Sand (%)	48.1	51.2
Silt (%)	41.8	34.7
Clay (%)	10.1	14.1

include carbonate species (CO_3^{2-} and HCO_3^-) and organic anions, the later are present in considerable amounts in soils rich in organic carbon.

3.2. WEOC and THM precursors in different pore size filtrates

The amounts of WEOC and THM precursors were proportional to the amounts of SOC. The SOC in Rindge Muck was 3.9 times higher than that of the Clay Loam. As expected, the Rindge Muck extracts contained more WEOC and THM precursors than the Clay Loam extracts. As seen in Fig. 2a, the WEOC in Rindge Muck extracts was 2.8–4.2 times higher than that of the Clay Loam extracts. In 1.2 μm filtrates, for example, 14.7 mg C and 5.3 mg C were extracted from 10 g of Rindge Muck and Clay Loam, respectively. With a higher concentration of WEOC, the Rindge Muck extracts had a higher THM formation potential than the Clay Loam extracts. A total of 1420 μg THM L^{-1} was formed in the 1.2 μm filtrates of Rindge Muck extracts, whereas a total of 420 μg THM L^{-1} was produced in the 1.2 μm filtrates of Clay Loam extracts. The amount of THM precursors in Rindge Muck was 3–4 times higher than the Clay Loam (Fig. 2b).

The amounts of WEOC decreased as pore size filters became smaller. This was simply due to the larger size organic matter being retained by the filters. However, the percentages of WEOC retained were different
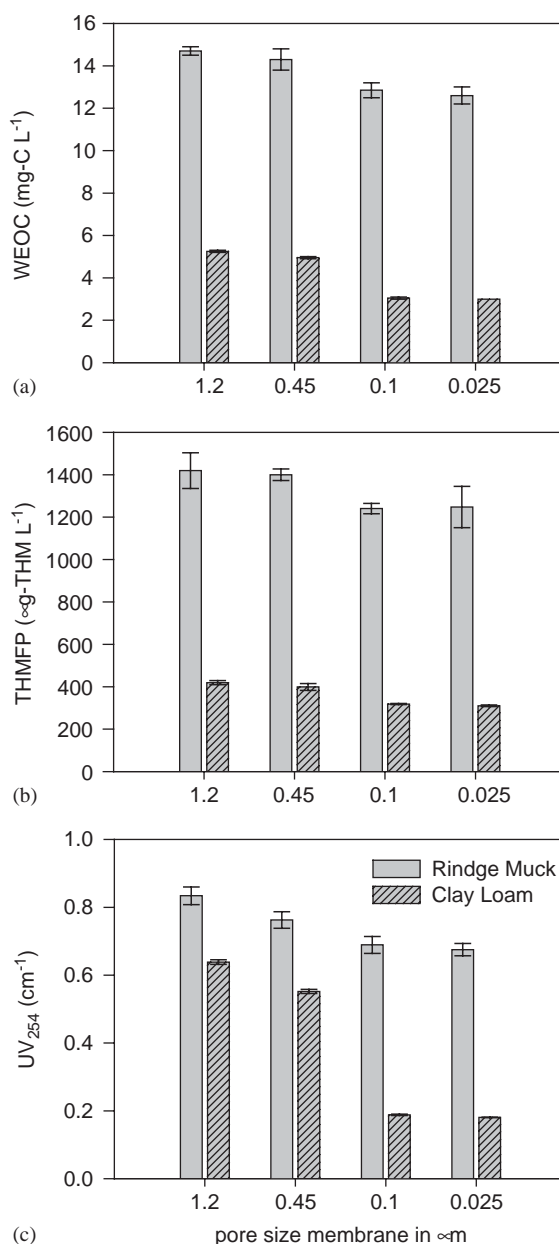

Fig. 2. WEOC, UV$_{254}$, and THMFP in filtrates of water extracts from Rindge Muck and Clay Loam soils. Error bar represents the range of the two replicates.

between the two soils. By examining the organic carbon retention from each pore size filter in Rindge Muck extracts, 2.7%, 12.2%, and 14.3%, of organic carbon was retained by 0.45, 0.1, and 0.025 μm filters, respectively. A total of 2.1 mg C L^{-1} was retained. In the Clay Loam extracts, 5.7%, 42%, and 43% of organic carbon was retained, respectively. A total of 2.3 mg C L^{-1} was retained. Particularly, significant amounts of WEOC in

the Clay Loam extracts passed through the 0.45 μm filter but were retained by the 0.1 μm filter, indicating that a large amount of organic carbon was in the 0.1 to 0.45 μm size range. In contrast, 0.45 μm filtrates of Rindge Muck extracts contained more homogeneous organic carbon and more than 85% of the organic fraction was smaller than 0.025 μm. We operationally defined the physical size of organic fractions with sizes of 1.2–0.45 μm, 0.45–0.1 μm, 0.1–0.025 μm, and smaller than 0.025 μm, as particulate, colloidal, fine colloidal, and dissolved organic carbon, respectively (Table 2).

Table 2
Definitions of organic fractions used in this study

Pore size	Organic fraction
1.2–0.45 μm	Particulate organic carbon (POC)
0.45–0.1 μm	Colloidal organic carbon (COC)
0.1–0.025 μm	Fine colloidal organic carbon (FCOC)
<0.025 μm	Dissolved organic carbon (DOC)

The WEOC and THMFP of individual organic carbon fractions can be determined by the differences between filtrates (Fig. 1). By this fractionation scheme, a significant amount of COC existed in Clay Loam extracts. More than 36% of the total WEOC was COC. DOC accounted for 57% of the total WEOC (Fig. 3b). In contrast, DOC was the major fraction in Rindge Muck extracts, more than 85% of the total WEOC (Fig. 3a). All other fractions were minor. In spite of differences in their abundances, the relative distribution of organic carbon fractions in extracts from both soils was similar: DOC $\gg$ COC > POC > FCOC.

The Clay Loam extracts contained 36% COC, but it accounted for less than 20% of THM formation; in contrast, the Clay Loam extracts contained 57% DOC, but it accounted for 74% of THM formation (Figs. 3b and d). The difference in WEOC and THMFP distributions implies that COC had a lower THMFP reactivity than DOC. Normalizing THMFP by the amount of WEOC in each fraction, we obtained the specific THMFP (STHMFP). For example, the STHMFP of
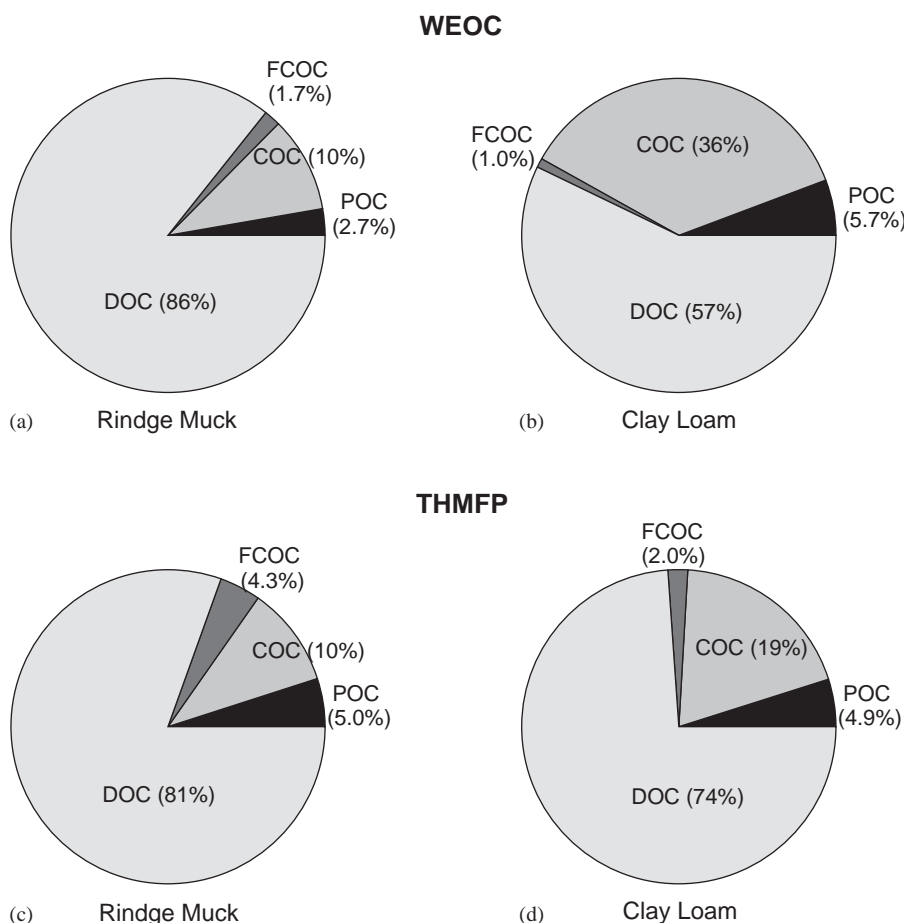

Fig. 3. Contributions of different organic fractions to WEOC and THMFP.

COC was equal to the difference in THMFP divided by the difference in WEOC between 0.45 μm filtrate and 0.1 μm filtrate. DOC in the Clay Loam had about 100 μg-THM mg C^{-1}, whereas COC had less than 50 μg-THM mg C^{-1}. Thus, Clay Loam DOC contains more THM precursor than Clay Loam COC. However, this difference in THM reactivity between COC and DOC was not observed in Rindge Muck extracts; their STHMFP were 110 and 100 μg-THM mg C^{-1}, respectively. Furthermore, there was no statistical difference in STHMFP between DOC from the two soils. Thus, we believe the 0.025 μm filtrate contains more homogeneous organic fractions that have similar chemical characteristics. On the other hand, 0.45 μm filtrate potentially contains heterogeneous COC, whose chemical behavior is source dependent.

Significant decreases in UV_{254} of Clay Loam extracts occurred when 0.45 μm filtrates were filtered through a 0.1 μm filter (Fig. 2c). Such a dramatic change did not

occur in WEOC and THMFP. We further examined the specific UV_{254} (SUV_{254}) and STHMFP and recognized a particularly high SUV_{254} but low STHMFP in the 1.2 and 0.45 μm filtrates of Clay Loam extracts (Figs. 4a and b). In contrast, higher STHMFP but lower SUV_{254} in 0.1 and 0.025 μm filtrates were recorded. This finding is contrary to the conventional wisdom that SUV_{254} is positively correlated with STHMFP. However, we noticed that 1.2 and 0.45 μm filtrates were cloudier than the other filtrates. The 1.2 and 0.45 μm filtrates had high turbidities, 21 and 16 NTU, respectively, compared to less than 0.5 NTU for the 0.1 and 0.025 μm filtrates. Turbidity blocks the light path when measuring UV absorbance, resulting in erroneously high absorbance at UV_{254}. Without the interference from light scatter by COC, the UV_{254} in 0.1 and 0.025 μm filtrates should be equal to the actual absorbance of organic molecules. Furthermore, similar SUV_{254} and STHMFP were recorded in all four filtrates of the Rindge Muck extracts. As discussed, COC was only a minor fraction (10%) in Rindge Muck extracts and its impact on turbidity was relatively small. Results indicated that UV_{254} and SUV_{254} in 0.45 μm filtrates are not necessarily proportional to chromophores from organic molecules or THM precursors and they can be affected by colloidal materials. Importantly, the potential for COC in water appears to be source dependent (e.g., organic vs. mineral soils). This partially explains why SUV_{254} is not always a good surrogate for STHMFP from various water sources.

3.3. Cation effects on WEOC and THM precursors

The presence of salt in extracting solutions decreased the amount of WEOC, but the magnitude of the reduction depended on the charge of the cation in the extraction solution and the type of soil being extracted (Figs. 5a and b). For example, the 1 dS m^{-1} Na^+ solution extracted 1.23 mg C g soil^{-1} in 0.025 μm filtrates from Rindge Muck. If the 0.025 μm WEOC filtrate (1.26 mg C g soil^{-1}) of the DW extracts is used as a reference, there was a 2.4% reduction for the 1 dS m^{-1} Na^+ extract. In contrast, 1 dS m^{-1} Ca^{2+} solutions extracted 0.63 mg C g soil^{-1}. This was a 50% reduction in WEOC relative to DW. Thus, the 1 dS m^{-1} Ca^{2+} solution reduced WEOC solubility more than the 1 dS m^{-1} Na^+ solution. Moreover, the different soil types behaved differently in the extraction process. The Clay Loam was more sensitive to the cation effect than the Rindge Muck. The 1 dS m^{-1} Na^+ solutions reduced WEOC by 23% and resulted in 0.23 mg C g soil^{-1} in the 0.025 μm Clay Loam filtrates. The Ca^{2+} solution was even more pronounced with the WEOC reduced by 78% in the 1 dS m^{-1} Ca^{2+} solutions and only 0.07 mg C g soil^{-1} extracted.
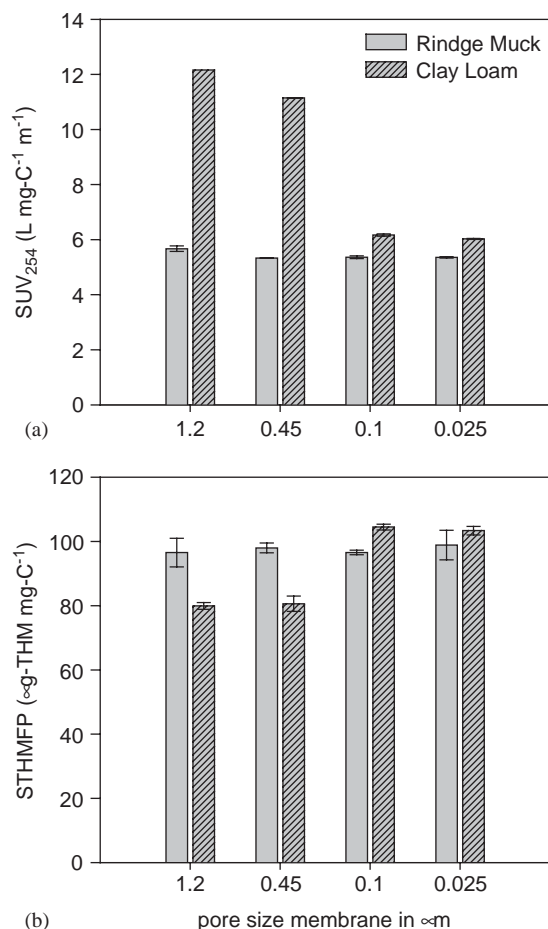

Fig. 4. SUV_{254} and STHMFP in filtrates of DW extracts from Rindge Muck and Clay Loam soils. Error bar represents the range of the two replicates.

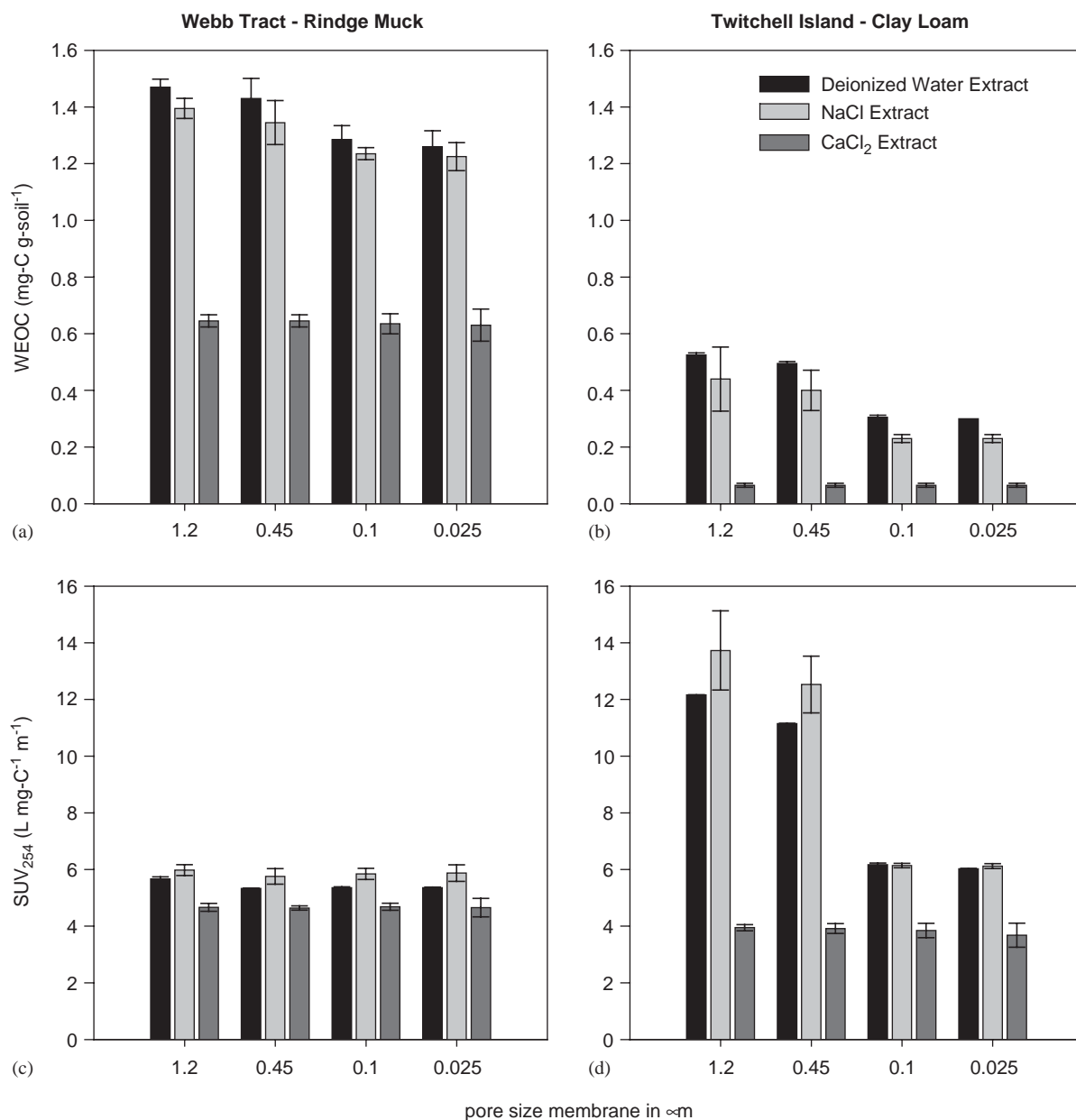Fig. 5. WEOC and SUV_{254} in filtrates of DW, NaCl, and $CaCl_2$ extracts from Rindge Muck and Clay Loam soils. Error bar represents the range of the two replicates.

Divalent cations are well known to be a more effective flocculant for humic substances than monovalent cations. Critical flocculation concentrations (CFC) for humic substances extracted from soils, defined as the minimum concentration at which flocculation starts, were found at 600 and 2.5–7.2 mM for Na^+ and Ca^{2+}, respectively (Ong and Bisque, 1968; Romkens and Dolfing, 1998). In this study, 10 mM Na^+ or 5 mM Ca^{2+} was used as extractant. This Na^+ concentration

was far below the CFC and the reduction of WEOC when passing through a series of filters was similar to that of DW extracts. The percentage of POC, COC, and FCOC did not change when Na^+ was added. Furthermore, complexation between DOC and Na^+ is minimal (Guo et al., 2001). Therefore the physical and chemical characteristics of DOC should be similar to that of DW extracts. In contrast, 5 mM Ca (Ca^{2+}) was in the range of CFC and a significant reduction in WEOC was

observed. The concentrations of WEOC decreased as a result of sorption and precipitation. Calcium ions are attracted to the negative carboxyl and hydroxyl groups in humic substances, which reduces their hydrophilic nature (i.e., water solubility) and/or provides a cation bridge that links humic substances to negatively charged soil surfaces (Ong and Bisque, 1968; Romkens et al., 1996). Moreover, there was no significant difference in WEOC among all four filtrates in Ca extracts, indicating that the physical size of WEOC is uniform. The POC, COC, and FCOC fractions were largely coagulated by Ca^{2+} and removed from the water resulting in only the DOC fraction 0.025 μm or smaller remaining. This DOC is not present as free organic molecules in water as it forms complexes with Ca^{2+} as small as 1 kDa (Guo et al., 2001; Romkens et al., 1996).

In addition, the percent reduction of WEOC from the two soils was different. Up to a 78% reduction of WEOC was found for the Clay Loam, whereas only a 50% reduction occurred for the Rindge Muck. Previous studies showed that Ca^{2+} results in preferential removal of high molecular weight (HMW) humic acid relative to lower molecular weight (LMW) fulvic acid (Tipping and Ohnstad, 1984; Romkens and Dolfing, 1998). The higher WEOC reduction in Clay Loam extracts implies that it may contain a higher proportion of HMW humic acid than the Rindge Muck. Equivalently, Rindge Muck may have a higher proportion of LMW fulvic acid. Results further imply that the WEOC passing through the 0.025 μm filter for Ca extracts contains only LMW fulvic acid. Indeed, the SUV_{254} in Ca extracts of both soils was lower than Na extracts, which is consistent with the conventional wisdom that humic acid has a higher SUV_{254} than fulvic acid (Croue et al., 2000). Neither filtration nor coagulation is able to remove this non-Ca^{2+} coagulated DOC fraction. Thus, DOC largely remains in water after pre-treatment in water facilities and reacts with disinfectants to form THM or other disinfection by-products during water disinfection. Further studies should focus especially on this fraction.

The cation composition of the extracting solution can affect SUV_{254}. Erroneously high SUV_{254} was recorded in 1.2 and 0.45 μm filtrates of Clay Loam DW extracts and Na^{+} solutions (Fig. 5d). In contrast, 1.2 and 0.45 μm filtrates of Ca^{2+} extracted from Clay Loam and 1.2 and 0.45 μm filtrates of Na^{+} or Ca^{2+} extracted from Rindge Muck had SUV_{254} similar to those in 0.1 and 0.025 μm filtrates (Figs. 5c and d). As previously discussed, this abnormally high UV absorbance was due to high turbidity caused by COC. A high proportion of COC was found in DW and Na^{+} solutions of the Clay Loam extracts. However, other soil extracts had a minor fraction of COC. The UV absorbance in these samples was mainly contributed by chromophores from organic carbon, rather than scattering by colloidal materials. Importantly, results indicate that the existence of COC

in water does not only depend on organic carbon sources (Rindge Muck vs. Clay Loam), but also depends on the type of cation in water. Agricultural practices, such as fertilizer and lime addition and salt leaching in the Sacramento-San Joaquin Delta alter salinity and sodicity and seasonally affect the composition of cations in soil waters. This in turn affects the composition of the organic fractions leaching from soils. Thus, water passing through a 0.45 μm filter potentially contains COC, depending on the source waters. The accuracy of SUV_{254} is uncertain if a 0.45 μm filtrate is used in the measurement. This is possibly one explanation for why poor correlations are sometimes obtained between STHMFP and SUV_{254} in various water sources (Fram et al., 1999).

The STHMFP of DOC from the two soils extracted by different electrolytes was similar to those extracted by DW (Fig. 6). As discussed for DW extraction, the STHMFP of both COC and DOC from Rindge Muck and the DOC from Clay Loam were about 100 μg-THM mg C^{-1}, but the STHMFP of COC from the Clay Loam was about half (50 μg-THM mg C^{-1}). The THM reactivity of individual organic carbon fractions did not change significantly with an increase of salinity or cation type in extracting solutions. The STHMFP of COC and DOC from all Rindge Muck extracts had an average of 99 and 102 μg-THM mg C^{-1}, whereas the STHMFP of COC and DOC from Clay Loam extracts had an average of 64 and 117 μg-THM mg C^{-1}, respectively. The STHMFP of DOC in Clay Loam extracts had a higher average than the STHMFP of DOC from Rindge Muck, but the difference was not significant ($p = 0.15$). Results implied that 0.025 μm filtrates contain DOC in which THM reactivity is source independent. Thus, it appears that a homogeneous organic carbon fraction can be collected with a filter having a 0.025 μm pore size. One of the drawbacks of using a 0.025 μm filter is the slow filtration rate. Our experiments found that there was less than a 5% difference in organic carbon and THM formation between 0.1 and 0.025 μm filtrates. Therefore, the use of a 0.1 μm filter may be more efficient for collecting a homogeneous organic carbon fraction.

4. Conclusion

Water extracts of representative organic and mineral soils from the Sacramento-San Joaquin Delta were filtered through a series of pore size filters (1.2, 0.45, 0.1 and 0.025 μm) and filtrates examined for TOC, UV_{254}, and THMFP. Results showed that the conventionally defined DOC (< 0.45 μm) potentially contains heterogeneous organic fractions, such as COC. COC was particularly important in extracts from the Clay Loam and it caused high turbidity that resulted in abnormally
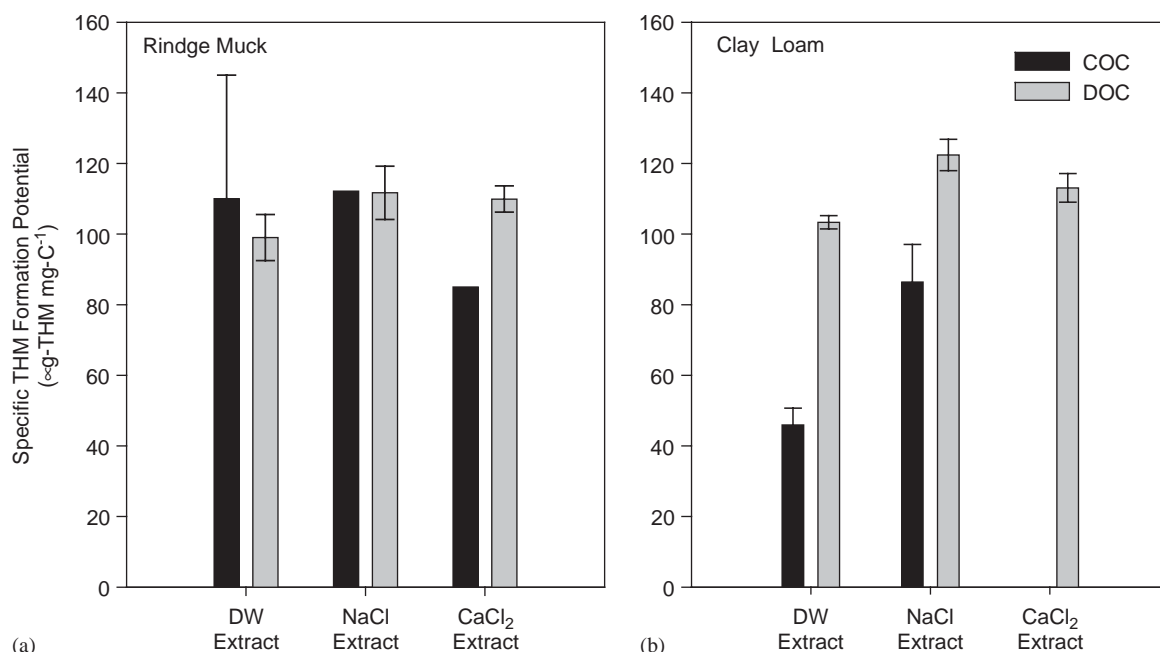
Fig. 6. The reactivity in THM formation of two major organic carbon fractions extracted with different electrolytes. Error bar represents the range of the two replicates.

high UV_{254} absorbance. There was no significant difference in STHMFP of the $<0.025\,\mu m$ filtrates from Clay Loam and Rindge Muck, but the STHMFP of COC from Clay Loam was about half that of COC from Rindge Muck. Moreover, specific conductance and cation type (especially charge differences) in extracting solutions can affect the amount and chemical composition of WEOC. Results imply that the quantity and quality of organic carbon in $0.45\,\mu m$ filtrates extracted from Delta soils can be seasonally dependent upon soil salinity and sodicity.

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